Suppression of the anomalous blue shift in the band gap temperature dependence of AgCuGaS$_2$ alloys

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It has been known for some time that, at temperatures below 100 K, the band gap of AgGaS$_2$ exhibits an anomalous *blue shift* with increase in temperature. We have found that this anomalous blue shift can be suppressed completely by as little as 1% of Cu in AgCuGaS$_2$ alloys. In conjunction with the disappearance of the blue shift, soft-phonon sidebands to the one-phonon Raman peaks are greatly broadened and no longer resolvable as distinct peaks. Our results are consistent with the suggestion that a soft-phonon mode may be responsible for this anomalous blue shift in AgGaS$_2$.

I. INTRODUCTION

It has been known[1–3] since the 1970s that the band gaps (E_g) of the Ag chalcopyrite semiconductors AgGaX_2 and AgInX_2 (where $X =$ S and Se) exhibit an anomalous blue shift with increase in temperature (T) for $T < 100$ K. For $T > 100$ K E_g shows the usual redshift with increase in T as found in most semiconductors. To our knowledge this behavior is not found in the diamond- and zinc-blende-type semiconductors, except in quantum wells and in GaInN alloys with large alloy fluctuations. In the latter cases the blue shift has been shown to be related to fluctuations in either the quantum well layer thickness or the band gap and the resultant localization of carriers at low temperatures.[4] The blue shift in such samples is observed only in the photoluminescence spectra and not in the absorption and reflection spectra. Furthermore, the magnitude of the blue shift is correlated with the inhomogeneous exciton linewidth caused by the potential fluctuations. So far no definitive explanation of this anomalous blue shift in the Ag chalcopyrites has been offered. Recently, it was suggested that this unusual behavior in AgGaS$_2$ may be related to the existence of a zone-edge soft-phonon mode in this compound.[5] Both the anomalous blue shift and the soft-phonon mode have been found to disappear in Ag$_x$Cu$_{1-x}$GaS$_2$ alloys containing 25% or more of Cu.[5,6] The fact that alloying tends to ''destroy'' the blue shift in AgGaS$_2$ is another indication that this phenomenon is different from the blue shift found in GaInN alloys. In this paper we have investigated the effect of a relatively small amount of Cu alloying on both the anomalous blue shift and the soft-phonon mode in the AgCuGaS$_2$ alloys. We found that both phenomena are suppressed by a Cu concentration of only 1%.

II. EXPERIMENTAL RESULTS

Our AgCuGaS$_2$ alloy samples were grown by the iodine vapor transport method. Details of the sample growth technique have been described elsewhere already and will not be repeated here.[7] The concentration of Cu in our alloys was varied by either 0.5% or 1% at a time by controlling the amount of Cu added to the starting materials. Temperature-dependent absorption measurements were performed with the sample located inside a variable-temperature helium refrigerator. The absorption and Raman measurements are similar to those described in previous publications.[6] The energy gap was determined from the absorption spectra using Eq. (5) in Ref. 8. The equation includes the contribution from both the bound and continuum states of the exciton to the absorption spectra. This approach takes into account the variation in the relative importance of the two contributions as a function of temperature. The energy of the band gap obtained in this way is plotted as a function of temperature in Fig. 1 for four Ag$_x$Cu$_{1-x}$GaS$_2$ alloys with $x = 1$, 0.995, 0.99, 0.98, and 0.97. The $x = 1$ (or 0% of Cu) curve has already been reported in Fig. 5 of Ref. 6. As found by several groups[1,3] including our own,[6] the band gap first increases with increase in temperature. Noting that this increase is almost linear in T, we have quantified this anomalous blue shift with a linear temperature coefficient (dE_g/dT) by fitting the band gap energy for $T < 100$ K with a straight line. Even a small amount of Cu has two very noticeable effects on the E_g vs T curves. The first effect is to suppress the band gap at $T \sim 0$ K. This is related to the large bowing parameter in the E_g vs alloy concentration curve, which has already been discussed in Ref. 6. The other effect is to suppress the anomalous blue shift. Although this blue shift is still observable in the $x = 0.995$ (or 0.5% of Cu) curve, the slope (dE_g/dT) has noticeably decreased. The blue shift disappears completely in the curves with $x \leq 0.99$ and there is nothing anomalous about these E_g vs T curves. The slopes (dE_g/dT) obtained from the $T < 100$ K curves are plotted as a function of x in Fig. 2. We should note that the slopes dE_g/dT for $T > 100$ K are all negative in the AgCuGaS$_2$ samples shown in Fig. 1 and their magnitudes are about a factor of 2.5 larger than the positive (dE_g/dT) at low temperature.
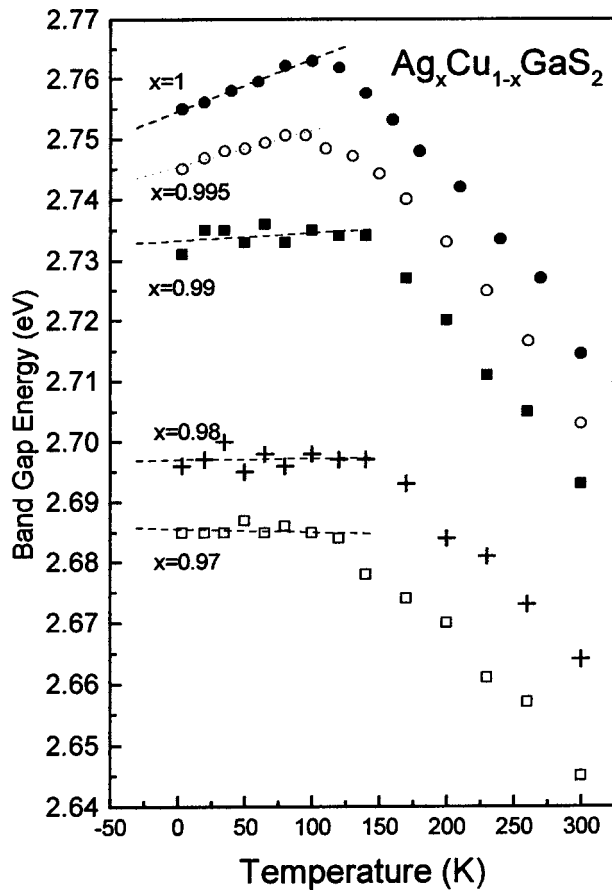
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FIG. 1. The temperature dependence of band gap energies in AgCuGaS$_2$ alloys for several low-Cu alloy concentrations. The broken lines represent linear fits to the band gap energies at low temperatures.

To investigate the effect of a small amount of Cu on the soft-phonon mode in AgGaS$_2$ we have measured the Raman spectra of our Ag$_x$Cu$_{1-x}$GaS$_2$ samples at 3.4 K. The resultant Raman spectra in the frequency range where soft-phonon modes have been observed are shown in Fig. 3. The $x=1$ spectrum is same as the one published already in Ref. 5. The vertical arrows in this spectrum point to the soft-phonon modes which appear as sidebands of the main one-phonon Raman peaks. These sidebands weaken gradually as the temperature is increased and disappear completely at $T > 100$ K.[5] Thus they disappear at approximately the same temperature as the anomalous blue shift. The detailed temperature dependence of these modes has been described in Ref. 5 and will not be repeated here. In the present work we demonstrated, in Fig. 3, that these sidebands due to the soft-phonon mode are suppressed by as little as 0.5% of Cu in the Ag$_x$Cu$_{1-x}$GaS$_2$ alloys. To see more clearly the difference between the $x=1$ and $x<1$ Raman spectra we expand the Raman spectra in the region between 380 and 410 cm^{-1} and normalize their peak intensities. The resultant spectra are shown in Fig. 4. The dashed arrows indicate the two soft-phonon mode sidebands in the $x=1$ spectrum. Although the $x=0.995$ and 0.99 spectra are almost identical, they differ from the $x=1$ spectrum in that they do not show any evidence of the soft-phonon mode sidebands. In addition, the
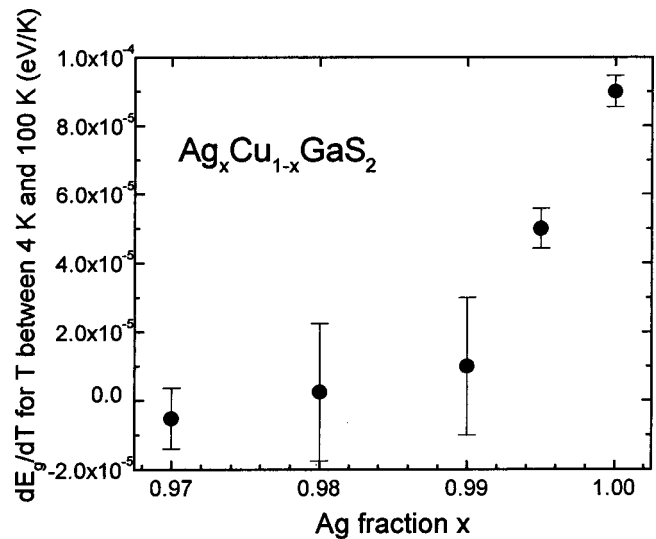

FIG. 2. The low-temperature linear temperature coefficients of the band gap energy in AgCuGaS$_2$ alloys plotted as a function of the Ag concentration in the alloys.

main Raman peak [which has been attributed to a $\Gamma_5(LO)$ phonon[9]] is significantly broadened. The net result is that the total integrated intensity contained in the main Raman peak and its soft-phonon sidebands in the $x=1$ spectrum is roughly the same as the total intensity of the broadened main peak in the $x<1$ spectra. A similar conclusion is obtained by analyzing the effect of Cu alloying on the other two Raman peaks and their soft-phonon sidebands in Fig. 3.
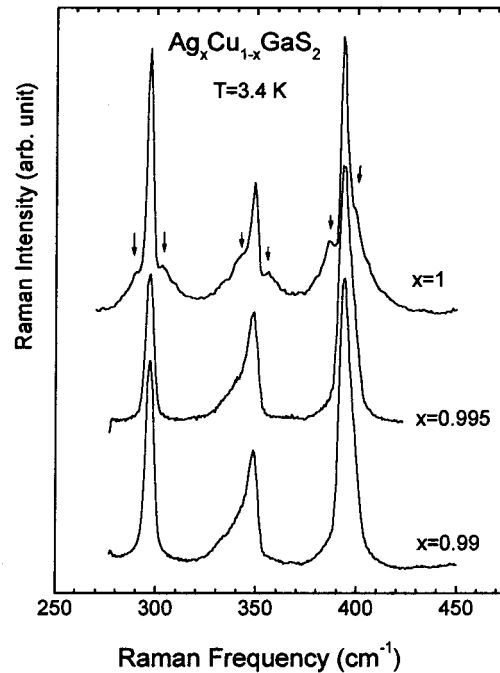

FIG. 3. The low-temperature Raman spectra in several AgCuGaS$_2$ alloys showing the high-frequency optical phonon modes and their soft-phonon sidebands (indicated by vertical arrows).
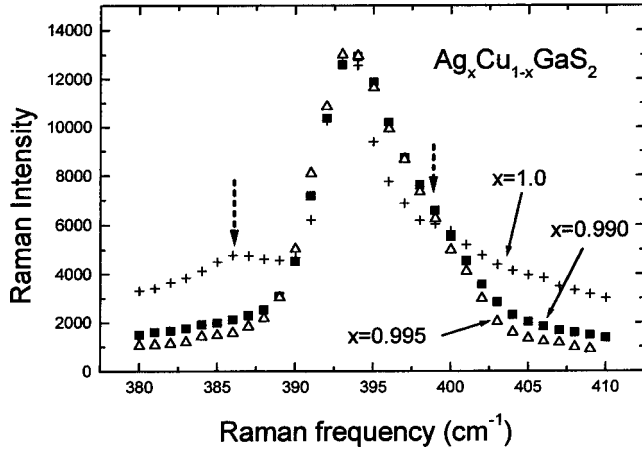
FIG. 4. A comparison between the Raman spectra around the $\Gamma_5(LO)$ peak in three different AgCuGaS$_2$ alloys. The peak intensity in the three spectra has been normalized. The dashed arrows point to the sidebands due to the soft-phonon mode in the $x=1$ spectrum.

III. DISCUSSION

In Ref. 6 it was pointed out that the temperature coefficient of the band gap (dE_g/dT) contains two contributions:

$$\left(\frac{dE_g}{dT}\right) = \left(\frac{\partial E_g}{\partial T}\right)_V + \left(\frac{\partial E_g}{\partial \ln V}\right)_T \left(\frac{d \ln V}{dT}\right). \quad (1)$$

The first term is due to electron-phonon interaction while the second term is associated with the dependence of the crystal volume on temperature (to be referred to as the thermal expansion term). The term $(\partial E_g/\partial \ln V)_T$ is known to be negative in most semiconductors including the chalcopyrites.[6] If the thermal expansion coefficient $d \ln V/dT$ is positive then the thermal expansion term is negative and hence cannot be responsible for the anomalous blue shift.

In Ref. 5 we suggested that the electron-phonon term can explain the anomalous blue shift of E_g if a low-frequency phonon mode (so far referred to as the soft-phonon mode) makes a significant contribution to $(\partial E_g/\partial T)$ at low temperatures only because this mode disappears with increase in temperature. If this explanation is correct then there should be a correlation between the soft-phonon mode and the anomalous blue shift. In the present paper we find that the anomalous blue shift is significantly decreased by about 0.5% of Cu and is completely absent for Cu concentration higher than 1%. The soft-phonon sidebands are not observable in the Raman spectra in AgCuGaS$_2$ samples containing more than 0.5% of Cu. However, the detailed comparison between the Raman linewidths and line shapes shown in Fig. 4 suggests that this soft phonon may still be present in the $x=0.995$ sample. It is not clearly observable in the Raman spectra of this sample mainly because of a *decrease in the frequency* of the soft-phonon mode with a possible increase in its damping so that the mode becomes overdamped. One evidence of this effect is the decrease in the strength of the phonon sidebands accompanied by an increase in the width of the strong one-phonon $\Gamma_5(LO)$ Raman peak in Fig. 4. As

a consequence of the overdamping of this soft phonon, its contribution to the anomalous blue shift via the electron-phonon term is decreased by a factor of 2 as shown in Fig. 2. For Cu concentration larger than 0.5% all one-phonon Raman modes are broadened further by alloy fluctuation so that phonon sidebands cannot be resolved in the Raman spectra of AgCuGaS$_2$.

We shall now consider the possibility that the anomalous blue shift may be caused by a reversal in the sign of the thermal expansion term at low temperature. In a diamond-type semiconductor, such as Si, it is known that the coefficient of thermal expansion is *negative* at low temperatures (i.e., $T<100$ K).[10] Since the coefficient of thermal expansion in AgGaS$_2$ at low temperatures has not been measured it is not known whether it is also negative at low temperatures. If it is negative at low temperatures as in Si then the second term in Eq. (1) can, in principle, also explain the anomalous blue shift. However, we shall argue that it is highly likely that this explanation can account for the large blue shift found in AgGaS$_2$.

First, we note that the negative coefficient of thermal expansion found in Si at low temperature is a rather weak effect. The magnitude of this low-temperature negative coefficient of thermal expansion is about one order of magnitude smaller than the positive coefficient of thermal expansion at higher temperatures. If one assumes that the coefficient $(\partial E_g/\partial \ln V)_T$ is independent of temperature then this negative coefficient of thermal expansion may produce a positive contribution to dE_g/dT that is at least one order of magnitude smaller than the magnitude of dE_g/dT at higher temperatures. We note that the magnitude of dE_g/dT in AgGaS$_2$ in the region of the anomalous blue shift is only about a factor of 2–3 smaller than the magnitude of the negative dE_g/dT at higher temperatures. Thus it is highly unlikely that this term can explain the large anomalous blue shift in this compound. In addition, the thermal expansion term accounts for only about 30% of the total value of dE_g/dT at higher temperatures.[6] In order to account for the anomalous blue shift in AgGaS$_2$ based on the thermal expansion term alone it would be necessary to assume that not only must its coefficient of thermal expansion at low temperature be negative but its magnitude has to be as large as the positive coefficient of thermal expansion at higher temperatures. This is a highly unlikely scenario. Thermal expansion is a manifestation of anharmonic coupling between lattice vibrations and the coefficient of thermal expansion and can be expressed in terms of the Grüneisen parameter of the phonon modes.[11] A large negative coefficient of thermal expansion would require the existence of one or more phonon modes with very large negative Grüneisen parameters. The frequency of such phonon modes would decrease as the sample is compressed and so their frequencies can be reduced to zero or near zero under sufficient compression. For this reason such phonon modes are often referred to as soft phonons. Thus we find that in either case it is necessary to postulate the existence of some soft-phonon modes in order to explain the anomalous blue shift in AgGaS$_2$.

We noted that a zone-center optical phonon in AgGaS$_2$ has been found by Carlone *et al.*[9] to become soft under high

pressure. It was pointed out by Artus *et al.*[12] that one way to understand the zone-center optical phonons in AgGaSe$_2$ is to start with the phonon dispersion of a zinc-blende structure crystal and to fold its Brillouin zone in half along the [100] (or X) direction. This folding of the Brillouin zone is justified by the doubling of the unit cube in the zinc-blende structure to form the tetragonal unit cell of the chalcopyrite structure. Thus the lowest-energy zone-center (Γ_{5T}) optical phonon in the chalcopyrite semiconductors corresponds to the low-energy zone-edge transverse acoustic (TA) mode along the X direction of the corresponding zinc-blende structure. It is now known that these zone-edge TA (X) modes in the zinc-blende structure have a tendency to go soft under pressure (i.e., negative Grüneisen parameters) and are responsible for the negative coefficient of thermal expansion in diamond- and zinc-blende-type semiconductors at low temperatures.[11] Considering the similarity between AgGaSe$_2$ and AgGaS$_2$ in terms of their bonding and chemical nature, one may expect to find also a soft zone-center phonon mode in AgGaS$_2$. However, the frequency of this soft phonon at atmospheric pressure (~ 34 cm^{-1}) is too high to explain the soft-phonon sidebands in the Raman spectrum shown in Fig. 3. Thus we propose that the soft phonon which is responsible for the anomalous shift in AgGaS$_2$ is probably a zone-edge TA phonon rather than the 34 cm^{-1} zone-center mode. Based on the idea of zone folding suggested by Artus *et al.*[12] in AgGaSe$_2$ we expect the zone-edge phonon in AgGaS$_2$ to have roughly one-half the frequency of the zone-center 34 cm^{-1} mode. This crude estimate puts the frequency of the soft-phonon sideband in the $x=1$ Raman spectrum in Fig. 3 at around half the value of the zone-center phonon, i.e., 17 cm^{-1}. This is in reasonable agreement with the experimental value of 8 cm^{-1} at 3.4 K since we expect the frequency of the phonon in the middle of the Brillouin zone to be suppressed as it becomes a zone-edge phonon as a result of zone folding.

A soft zone-center optical phonon exists also in CuGaS$_2$ and probably in other chalcopyrite compounds as well. However, the frequency of this soft phonon in CuGaS$_2$ (74 cm^{-1}) is twice as high as in AgGaS$_2$ and its Grüneisen parameter is five times smaller in magnitude.[9] Presumably this is also true for the soft zone-edge phonon in CuGaS$_2$. The higher frequency of such modes in CuGaS$_2$ probably results in a much weaker electron-phonon coupling and explains why the anomalous blue shift is not observed in CuGaS$_2$ in spite of the great similarity between its optical properties and those

of AgGaS$_2$. The reason why such a zone-edge soft-phonon mode would be so sensitive to a small amount of Cu can be explained by the fact that these modes involve mostly motion of the heaviest atom in the chalcopyrite structure, namely, the Ag atoms. This was demonstrated theoretically by Artus *et al.* for AgGaSe$_2$.[12] Since S atoms are lighter than Se atoms this conclusion should be even more valid for AgGaS$_2$. When the Ag atoms are replaced by the much lighter Cu atoms we expect two things to occur. First, for small concentrations of Cu, the soft-phonon mode will be strongly scattered as a result of alloy fluctuation leading to overdamping of these modes as we observed in the Raman spectra shown in Fig. 4. For still higher Cu concentrations a separate higher-frequency zone-edge soft-phonon mode involving mainly vibration of the Cu atoms will emerge. This higher-frequency mode presumably has a much weaker coupling to the band gap electrons and hence does not produce an anomalous blue shift in the AgCuGaS$_2$ alloys with Cu concentrations higher than 25%.[5] In this regard the behavior of the zone-edge soft-phonon mode in CuGaS$_2$ and in AgCuGaS$_2$ alloys with large Cu concentration is similar to that found in zinc-blende-and diamond-type semiconductors.

IV. CONCLUSIONS

In conclusion, we have found that the anomalous temperature-dependent blue shift in the band gap of AgGaS$_2$ at low temperature is suppressed completely by as little as 1% of Cu. Together with the disappearance of this blue shift the soft-phonon mode that has been observed as sidebands of strong one-LO-phonon Raman peaks is also broadened and weakened by alloying with Cu. Our results are consistent with the proposal that the existence of such a soft-phonon mode in AgGaS$_2$ may be responsible for the anomalous blue shift in the band gap of AgGaS$_2$ at low temperatures.

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